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## Heat Evolution of Cement.

CONTROL BY THE USE OF REAGENTS.

A PAPER by Mr. L. R. Forbrich, published in the *Journal of the American Concrete Institute* for November, 1940, describes a method of controlling the heat evolution of cements by the addition of small quantities of active reagents. Data are presented showing the effects of a dispersing agent, an inorganic accelerator, an organic catalyst, and various combinations of these reagents, on the heat liberation characteristics of several cements. Data also are presented showing the effects on the strength, durability, and shrinkage of concrete of three combinations of the reagents which appeared to have practical value. One of these combinations was designed specifically for concrete in which heat evolution, particularly at the early ages, is important, and the other two were designed for use in ordinary concrete.

In the course of the paper the author states that the significance of early rates of heat liberation has not received a great deal of attention, but preliminary studies made by Mr. R. W. Carlson<sup>1</sup> by means of a conduction calorimeter showed that different cements had vastly different early heat-liberation characteristics. In *Fig. 1* are shown the early-heat-liberation characteristics of four different types of Portland cement—namely, a standard, high-early-strength, modified, and low-heat cement. It was also found that the early rates were affected by many variables, of which the most significant were fineness, chemical composition, gypsum, cooling rate of clinker, temperature, admixtures, and certain chemicals. Evidence was found that the early rates of heat liberation may be related to setting time and early strength, as well as to temperature rise in concrete.

The inferences to be drawn from this investigation by Mr. Carlson and the results of a few exploratory tests indicated that there might be other and more

satisfactory means of controlling the early-heat-liberation characteristics of the cement than the method of changing the composition, namely, through the addition of small amounts of active reagents. To determine the possibilities which this method offers, an investigation was undertaken to evaluate the effects, on the heat liberation characteristics of cement and of two pure cement compounds, of certain reagents whose effects on the physical properties of concrete were already fairly well known. These reagents consisted of a dispersing agent, an inorganic accelerator, and an organic catalyst.

It is known that dispersing agents increase the number of discrete particles of cement available for hydration, that is, increase the available specific surface, which in turn leads to a reduction in water required for a given workability, increased strength and increased durability. An attempt was made to study the influence of calcium lignin sulphonate.

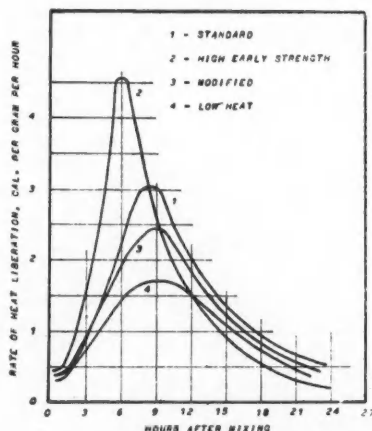


Fig. 1.—Typical Early-Heat-Liberation Rates of Different Types of Portland Cement.

Certain inorganic compounds affect the rate of setting and hardening of cement. It appears obvious that a compound which accelerates hardening will increase the early rate of heat evolution, but it seemed desirable to check this and a few determinations were made with calcium chloride. A number of organic materials will impair or prevent the hardening of cement, but other organic materials used in very small proportions will materially increase the strength of concrete. Such a material may be termed a catalyst since, in the proportions used, it cannot have a significant effect on strength by direct combination with any part of the cement. It must therefore promote some reaction of the cement in which the compound itself takes no part, or at least only an intermediate part. One group of such compounds, which may be described as substituted hydroxybenzoic acids, has the property of increasing the rate of strength gain after

3 to 7 days without materially affecting the early strength. It might be inferred that such a material would not materially alter the heat evolution at early ages but would increase it at later ages and would also increase the total heat evolution. Since the mechanism of the reaction is still obscure it by no means follows that this is the case and, therefore, determinations of heat evolution were made with ortho-hydroxy benzoic acid.

TABLE A  
MIXTURES

Identification No.	Composition—Parts per Unit Weight			
	Dispersing Agent	Accelerator	Organic Catalyst	Pozzualana
1	.30	0	0	.70
2	0	1.00	0	0
3	0	0	.075	.925
4	.30	.25	0	.45
5	.30	.50	0	.20
6	.30	0	.075	.625
7	.30	0	.050	.65
8	.20	0	.075	.725
9	.30	.50	.075	.125
10	.30	.25	.075	.375
11	.30	.25	.050	.400

NOTE—The admixtures were used in the amount of 1.065 per cent by weight of the cement (one pound per sack).

The proportions of the reactive agents used were determined by their effects on properties other than heat evolution. The dispersing agent was used up to 0.32 per cent. by weight of the cement, since the plasticising or water-reducing action increases but slightly with greater proportions. The accelerator (calcium chloride) was used in amounts up to 1 per cent. of the weight of the cement, since this proportion is effective as an accelerator and is not deleterious. The organic catalyst was used in proportions of 0.053 per cent. and 0.080 per cent., which had been determined to be most efficient in increasing strength. For routine experimental convenience, these reagents were used intermixed with fly ash, which, in the small quantities used, was found to have no measurable effect on early heat liberation.

#### Materials.

Six cements were furnished by a cement research laboratory and four cements were purchased in Cambridge, Mass.

Scituate sand and gravel, air dried and graded, and crushed limestone were used.

The mixtures are given in *Table A*.

#### Test Methods.

**RATE OF HEAT LIBERATION.**—The early rates for cements were measured by means of a conduction calorimeter<sup>1, 2</sup> on pastes of 0.35 water-cement ratio by weight. Essentially the method consists in observing small temperature differences between the ends of a conducting metal tube of which one end is connected to a copper core inserted in the specimen and the other end maintained at about constant temperature (75 deg. F.). Temperature differences are measured to

within 0.02 deg. C. by resistance thermometers and a special resistance test set. Since the heat is conducted away from the specimen almost as fast as it is liberated it is possible to determine the rates of heat liberation of the cements at approximately constant temperature.

**HEAT OF HYDRATION.**—Determinations were made by means of a simplified heat of solution calorimeter.<sup>2, 3</sup> The cement pastes were placed in glass vials which were stoppered, sealed, and then stored at 75 deg. F. until tested. Except where the water-cement ratio was a variable, the water content of the paste was 0.40 by weight.

**CONCRETE TESTS.**—Cylinders were cast from each mix according to standard methods. For compressive strength tests the specimens were either 3 in. by 6 in. or 6 in. by 12 in. cylinders. The specimens for durability and shrinkage were 3 in. by 6 in. cylinders equipped at each end with stainless steel gauge points. Length change measurements were made by means of a Federal dial comparator. After the curing period the shrinkage specimens were placed in air of 50 per cent. relative humidity and the specimens for durability were subjected to cycles of freezing, thawing, and heating. Each cycle consisted of the following treatment: (1) Cooling the saturated specimen in water at 32 deg. F. for two hours; (2) freezing at 15 deg. F. for 14 to 16 hours; (3) heating in water at 165 deg. F. for two hours; (4) cooling in water at 75 deg. F.

### Results of Tests.

**EARLY RATE OF HEAT LIBERATION.**—Since the chemical composition of cement has an important bearing upon both the rate and total amount of heat liberation, it was decided to study the effect of the dispersing agent, the accelerator, and the organic catalyst on the two pure compounds tricalcium aluminate ( $C_3A$ ) and tricalcium silicate ( $C_3S$ ) which are largely responsible for heat liberation during early periods of hydration.  $C_3A$  liberates more heat per unit weight than any other major compound, and this occurs almost entirely within the first 24 hours.  $C_3S$ , on the other hand, liberates heat much more slowly during the first 24 hours, but since it is present in much larger quantities it may actually contribute more heat than the  $C_3A$ .

The  $C_3A$  used in these experiments was ground with 12 per cent. gypsum to a surface area of 1,565 sq. cm. per gramme. This amount of gypsum, which was necessary to prevent too rapid setting, corresponds approximately to the proportions per unit of  $C_3A$  that exist in cement. It is believed that the presence of the gypsum would affect mostly the time at which maximum heat generation occurs and would not influence the relative effects of the active agents. The  $C_3S$  was ground without additions to a surface area of 1,620. The reagents, except the calcium chloride, were added with the pozzolanic material (fly ash); the amounts of reagents used, by weight of the cement or of pure compounds, were as follows: dispersing agent, 0.32 per cent.; organic catalyst, 0.08 per cent.; calcium chloride, 1.0 per cent.

The results of the tests made on tricalcium aluminate are presented in Fig. 2. The addition of the dispersing agent delayed the occurrence of the point of

maximum heat liberation by about 14 hours, while the organic catalyst and the accelerator (calcium chloride) shortened slightly the time before the maximum rate of heat liberation. Within the limits of experimental error these active agents had no appreciable effect on the maximum rate of heat evolution or on the total heat evolved during the first 24 hours.

The results of tests made on tricalcium silicate (*Fig. 2*) show that the dispersing agent greatly retarded the heat generation, at least during the first 27 hours, so that there was only a small amount of heat evolution up to that time. The organic catalyst also had a retarding effect, but it was considerably less than for the dispersing agent. It delayed the time of maximum heat generation by eight to ten hours but did not affect the total heat evolved in 27 hours. Calcium chloride had a marked accelerating effect on  $C_3S$ ; it increased the maximum rate

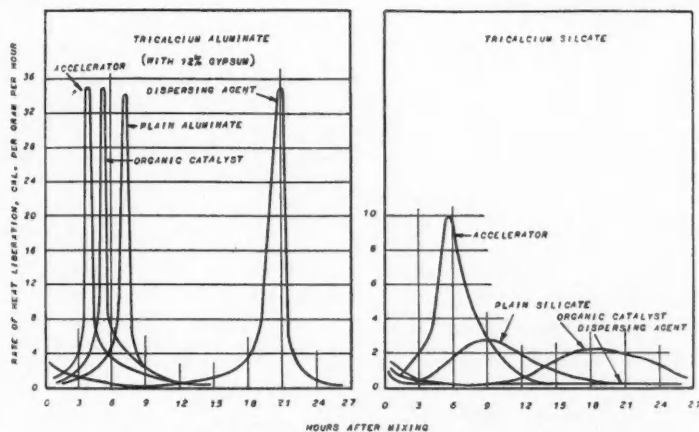


Fig. 2.—Effect of Reagents on Heat Liberation Rates of Tricalcium Aluminate and Tricalcium Silicate.

of heat generation almost five times, shortened slightly the time to reach this maximum, and increased the total heat evolved by more than 50 per cent. during the first 24 hours.

The effects of the three active compounds on the heat liberation characteristics of two standard Portland cements are shown in *Fig. 3*. For both cements, calcium chloride had an accelerating effect as shown both by the increase in the maximum rate of heat generation and by the shortening of the time required for attainment of this maximum. The dispersing agent, on the other hand, had a retarding effect. For cement L the heat curve was flattened considerably; the maximum rate was almost halved so that the heat curve somewhat resembled that for a low-heat cement (*Fig. 1*). For cement U, which has a lower  $C_3A$  content than cement L, the retarding action of the dispersing agent was greater. In this case the maximum rate of heat generation did not take place until after



about 30 hours. The effects of the organic catalyst were small; in both cases, it produced some retardation.

**COMBINATION OF REAGENTS.**—The results of tests on the three active reagents with two pure cement compounds and with two Portland cements indicated that these reagents had definite influences on the early rates of heat evolution. The dispersing agent had a retarding effect, the calcium chloride an accelerating effect, and the organic catalyst apparently only a small retarding effect. From these results it seemed that it would be possible to control the heat liberation characteristics of cement to any desired degree by the use of varying combinations of the three reagents. With this objective the effects of eight different combinations of the three reagents were studied on several different Portland cements. The combinations, the compositions of which are given in *Table A* and on the diagrams, were added in the amount of 1.065 per cent. by weight of the cement.

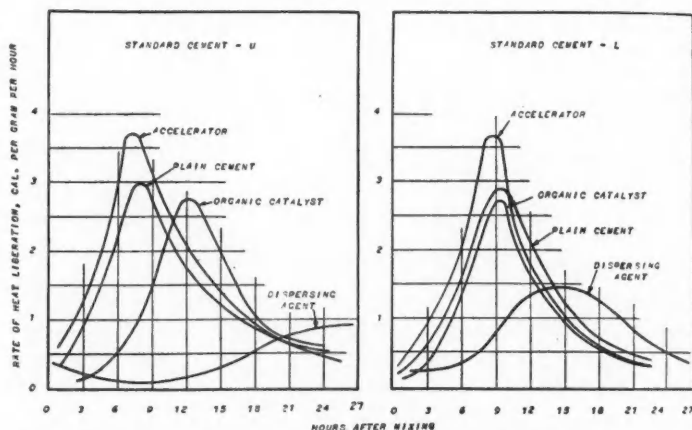


Fig. 3.—Effect of Reagents and Combinations of Reagents on Heat Liberation Rates of two Standard Portland Cements.

**Dispersing Agent and Accelerator.**—In *Fig. 4* are shown the effects of the dispersing agent alone, and in combination with two quantities of calcium chloride, on the early rate of heat liberation of two standard Portland cements. For both cements the accelerator compensates to different degrees the retarding action of the dispersing agent. With 0.50 part calcium chloride added the retarding action of the dispersing agents on cement L is almost completely compensated (curve 5), so that the heat curve is about the same as for the plain cement. With cement U it is clear that more than 0.50 part calcium chloride would be required to offset completely the retarding effect of the dispersing agent.

**Dispersing Agent and Organic Catalyst.**—In *Fig. 5* the effect of the organic catalyst on the action of the dispersing agent is shown for two cements. The action of the organic catalyst increases the extent of retardation of the dispersing



agent for both cements (curves 6 and 7). On cement U the combined effects of dispersing agent (0.30 part) and organic catalyst caused extreme retardation during the first 24 hours. By reducing the quantity of dispersing agent, retardation, as would be expected, was lessened (curve 6) but small differences in amounts of organic catalyst had a negligible effect.

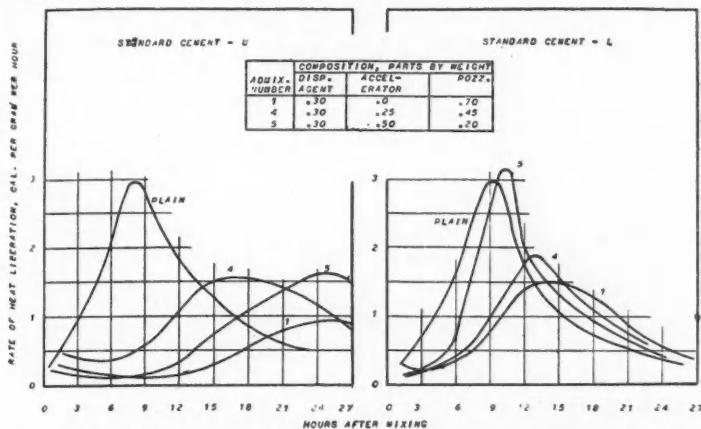


Fig. 4.—Effect of Reagents and Combinations of Reagents on Heat Liberation Rates of Two Different Portland Cements.

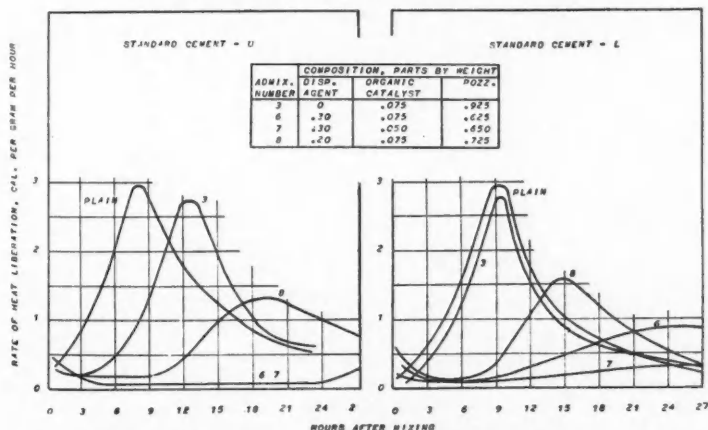


Fig. 5.—Effect of Reagents and Combinations of Reagents on Heat Liberation Rates of Two Different Portland Cements.

*Dispersing Agent, Organic Catalyst, and Accelerator.*—Fig. 6 shows the effects of combinations of the three reagents on two cements. For cement U the retardation produced by the dispersing agent and organic catalyst was so great that the effects of additions of different amounts of calcium chloride were

indistinguishable. With cement L the effects of the combinations are more clearly shown. The effect of 0.50 part of accelerator was to influence the retarding action of the other reagents to the extent that the maximum rate of heat evolution was increased beyond that of the plain cement, although the beginning of rapid heat evolution was delayed slightly. With a smaller amount of accelerator the retarding effects of the other reagents was only partially compensated, as would be expected. The curves obtained for the combinations with two different proportions of organic catalyst do not seem to be consistent with other data obtained.

*HR-0, HR-10, HR-20.*—The results of the tests on the effect of different combinations of accelerator, dispersing agent, and organic catalyst prompted further detailed studies on three combinations which showed evidence of practical value. The three combinations selected were named HR-0, HR-10, HR-20,

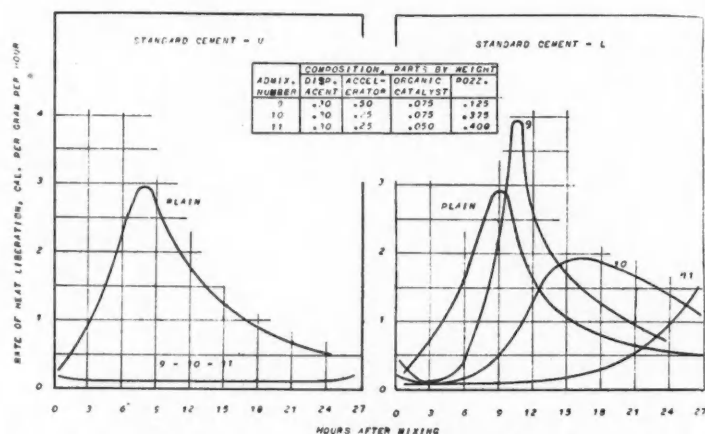


Fig. 6.—Effect of Reagents and Combinations of Reagents on Heat Liberation Rates of Two Brands of Portland Cement.

TABLE B

Name	Composition—Parts by Weight			
	Dispersing Agent	Accelerator	Organic Catalyst	Pozzuolana
HR-0	.30	.50	0	.20
HR-10	.30	.50	.075	.125
HR-20	.30	0	.075	.625

and had the compositions as in Table B. HR-0 was designed for ordinary construction work where heat evolution is not of importance but where the effects of a dispersing agent on the other properties of concrete and normal hardening rates are desired. HR-10 was proportioned for similar application where the effect of the organic catalyst in producing increased strength at the

later ages as well as the effects of the dispersing agent are important. HR-20 was designed for work in which heat evolution, particularly at the early ages, is the primary consideration.

HR-0.—In Figs. 7 to 10 the effect of HR-0 on the early rates of heat liberation of seven different cements are presented. For the standard Portland cements

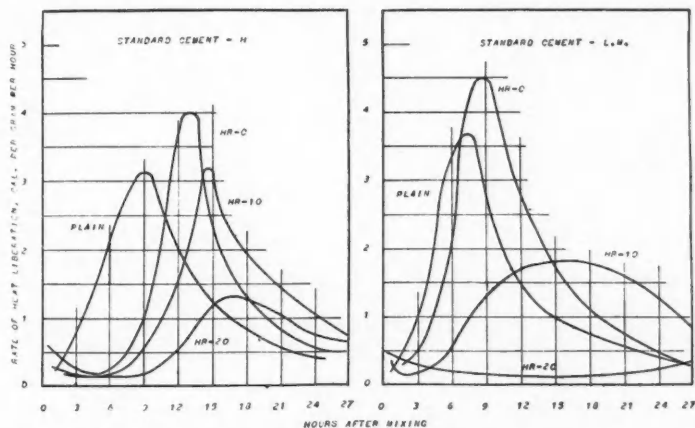


Fig. 7.—Effect of Three Combinations of Reagents on Heat Liberation Rates of Different Portland Cements.

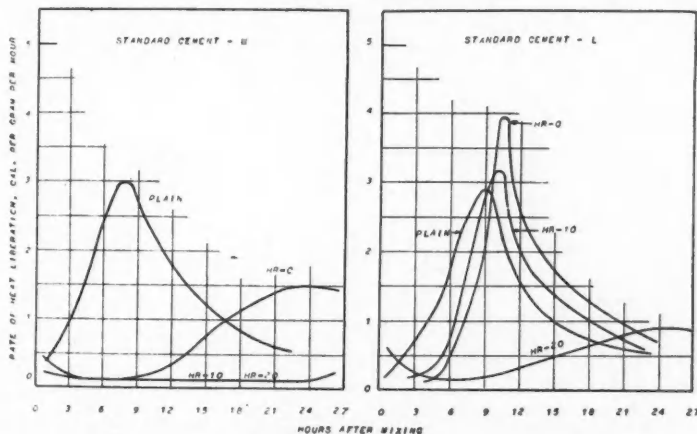


Fig. 8.—Effect of Three Combinations of Reagents on Heat Liberation Rates of Different Types of Portland Cement.

(Figs. 7, 8 and 9) HR-0 generally delayed the time at which rapid heat evolution occurred; for one cement (Fig. 9), however, there was a small accelerating effect. The influence of this material on total heat liberated up to one day was small; in one case only was there any significant effect, and that was for cement LM,

which showed an increase of about 5 to 7 calories. In Fig. 10 the effect of HR-o on a modified and on a sulphate-resisting cement are shown. As for the standard cements, the start of rapid heat evolution was delayed but the maximum rates in both cases were increased so that in 36 hours the total heat evolved was not materially affected.

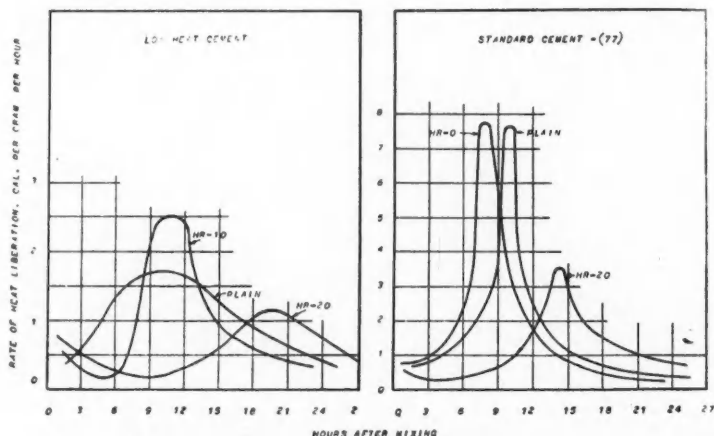


Fig. 9.—Effect of Three Combinations of Reagents on Heat Liberation Rates of Different Types of Portland Cement.

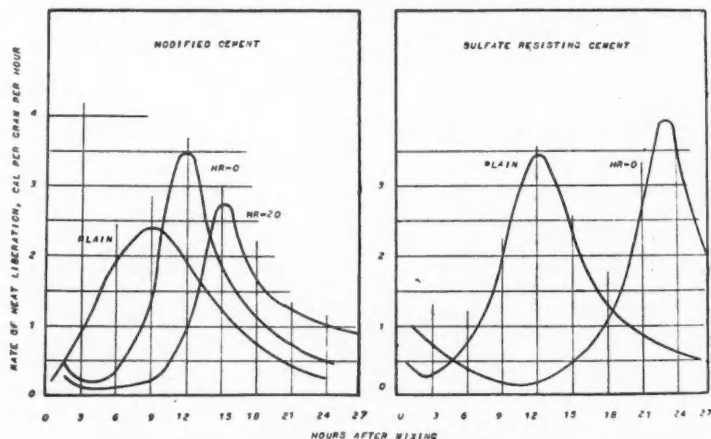


Fig. 10.—Effect of Three Combinations of Reagents on Heat Liberation Rates of Different Types of Portland Cement.

In general it was evident that, from a practical point of view, HR-o did not greatly affect the heat liberation characteristics or the early hardening properties of the cements. In a few cases somewhat more retardation than would be

desirable was observed, but this may be readily overcome by increasing the proportion of accelerator. HR-o, therefore, would be suitable for ordinary construction purposes and would provide the benefits of the dispersing agent without materially altering the hardening rate or heat characteristics of the concrete.

*HR-10.*—In *Figs. 7, 8 and 9* the effects of HR-10 on the early-heat-liberation characteristics of five cements are shown. The effects of this material were similar to those of HR-o, except that in general it caused slightly more retardation. For cement U (*Fig. 8*), which contains 6.5 per cent.  $C_3A$ , somewhat less than that found in most normal cements, the retardation caused by HR-10 appeared to be excessive.

*HR-20.*—In *Figs. 7 to 10* the early heat curves for HR-20 with several different types of cement are shown. The effect of this material was consistently to delay the time to reach maximum heat generation and to reduce both this maximum rate and the total heat evolved during the first 24 hours. The test data show that HR-20 will accomplish its intended purpose of decreasing heat evolution during the first 24 hours with any type of Portland cement. For some of the cements it might be necessary to modify the composition of HR-20 to make it of practical value. The fact that HR-20 apparently retarded the hydration process of the cements might indicate that it would also impair early strength. However, concrete tests showed that this was not the case.

The early heat liberation tests with HR-o, HR-10 and HR-20 showed that within limits the three active reagents can be combined so as to control the heat liberation characteristics of cement as desired, but that the influence of the reagents varied with different cements. An attempt was made to determine what constituents in cement were responsible for these variations, but this was not successful. The data indicate, nevertheless, that cements low in  $C_3A$  and possibly high in  $C_3S$  are retarded to the greatest degree by the dispersing agent and the organic catalyst. The influence of minor constituents may, on the other hand, have more influence than would ordinarily be expected. It might be necessary to adjust slightly the compositions of materials HR-10 and HR-20 for use with some cements.

*Heat of Hydration.*—The effect of HR-o on the heat of hydration of seven different cements is shown in *Table 1A*. It will be seen that HR-o increased slightly the heat of hydration of most cements at three days; the average increase for all the cements was 2.3 calories per gramme. At the age of seven days there was still a small increase due to HR-o (average 1.7 calories), but at 28 days no consistent differences were found. In general it can be said that HR-o slightly increased the heat of hydration at the early ages but had no effect at the later ages.

The influence of HR-10 on the heat of hydration of three cements is given in *Table 1B*. The data are limited, but since the observed differences are small it appears that the material behaves in about the same manner as HR-o, except that there is some indication of a small retarding effect at three days rather than a small accelerating effect.

In *Table 1A* data showing the effect of HR-20 on the heat of hydration of

TABLE I-A—EFFECT OF HR-0 ON HEAT OF HYDRATION

Cement	Admixture	Heat of Hydration—Cal. per Gram of Cement			
		3 Days	7 Days	28 Days	110 Days
Standard L.M.	Plain	70.3	85.4	103.5	.....
	HR-0	71.3	88.0	99.2	.....
Standard H	Plain	64.8	80.7	91.3	.....
	HR-0	64.8	80.7	90.9	.....
Standard (77)	Plain	65.3	77.2	92.2	.....
	HR-0	67.9	77.2	92.8	.....
Standard (91)	Plain	77.5	84.8	97.1	.....
	HR-0	79.7	90.1	99.0	.....
High Early	Plain	71.7	84.4	91.8	.....
	HR-0	75.1	84.9	92.7	.....
Modified	Plain	53.5	64.8	77.1	.....
	HR-0	56.7	65.8	76.0	.....
Sulphate Resisting	Plain	56.7	69.2	77.3	.....
	HR-0	60.2	71.9	78.8	.....

TABLE I-B—EFFECT OF HR-10 ON HEAT OF HYDRATION

Standard L.M.	Plain	70.3	85.4	103.5	112.5
	HR-10	66.6	83.2	97.2	106.5
Standard H	Plain	64.8	80.7	91.3	98.6
	HR-10	61.6	83.9	91.5	101.0
High Early	Plain	71.7	84.4	91.8	97.4
	HR-10	72.3	85.9	93.0	104.0

TABLE I-C—EFFECT OF HR-20 ON HEAT OF HYDRATION

Cement	Admixture	Heat of Hydration—Cal. per Gram of Cement			
		3 Days	7 Days	28 Days	110 Days
Standard L.M.	Plain	70.3	85.4	103.5	112.5
	HR-20	49.4	78.3	103.5	108.9
Standard H	Plain	64.8	80.7	91.3	98.6
	HR-20	63.3	83.2	97.7	111.0
Standard L	Plain	81.6	92.6	102.0	107.2*
	HR-20	35.6	77.9	104.8	109.8*
Standard (77)	Plain	65.3	77.2	92.2	97.9
	HR-20	58.1	76.1	103.8	104.5
Standard (91)	Plain	77.5	84.8	97.1	109.2
	HR-20	61.3	90.0	109.5	112.8
Modified	Plain	53.5	64.8	77.1	91.3
	HR-20	52.5	61.3	75.4	94.1
Sulphate Resisting	Plain	56.7	69.2	77.3	85.9
	HR-20	39.9	60.7	83.7	88.2

\*60 Days.

NOTE—HR-0 added in amount of 2.13 per cent; HR-10 and HR-20, 1.065 per cent by weight of cement. Water-cement ratio 0.40 by weight. Curing temperature, 75°F.

seven cements are presented. At the age of three days, HR-20 reduced the heat of hydration for all cements. For two cements this reduction amounted to one or two calories but for the others it varied from 10 to 50 per cent. of the heat liberated by the plain cement. At seven days the heat of hydration was reduced for five cements, and at 28 days only one cement showed a reduction in heat of hydration due to HR-20; the others showed increases of as much as 12 per cent. of the total heat evolved by the plain cement. At 110 days most of the cements showed increased heat of hydration due to HR-20, but the increases were smaller than at 28 days.

At three days the effect of water-cement ratio on the heat of hydration of the two cement pastes with and without HR-o is small but at seven and 28 days it was significant. At 28 days for an increase in the water-cement ratio of 0.10 there is an increase in heat of hydration of 4 to 6 calories for the normal cement and 2 to 4 calories for the modified cement. This applies to the plain cement pastes and to pastes with HR-o as well. These effects of water-cement ratio were smaller (about one-half) than those reported by previous investigators.<sup>4, 5</sup>

#### Concrete Tests.

Although there were some inconsistencies in the strength data, the addition of the three materials generally produced increases in strength corresponding approximately to the reduction in water-cement ratio permitted by their use. In these tests the average reduction in water-cement ratio for all the mixes was 13 per cent., but it is clear that the water requirement for a given consistency depends on many variables such as type of mixing, gradation of aggregate, design of mix and others.

Since HR-o and HR-10 were designed to have no appreciable effect on the early hardening properties it would be expected that the early strength increases would be in accord with the reduction in water-cement ratio. In the case of HR-10, which contains the organic catalyst effective beyond seven days, it would be expected that the increase in strength at the later ages would be somewhat greater than that which would be obtained by the reduction in water-cement ratio permitted. These effects, in general, are realised.

In the case of HR-20, which showed a retarding effect on the early rate of heat evolution of neat cements, the compressive strength of the concrete was increased to a small degree at the early ages (three days). At the intermediate ages the strength increases were in accord with the reduction in water-cement ratio, and at the later ages the increases were slightly greater than would be expected from the water reduction. It is apparent that at early ages the retarding effect of HR-20 was largely or entirely offset by the physical effect of the reduction in water-cement ratio, while at the later ages there is some evidence that the organic catalyst had a beneficial influence.

The strength-heat ratio expressed as the ratio of compressive strength to heat of hydration is in some respects a measure of the efficiency of a cement for mass concrete construction. The strength-heat ratio has been shown by previous investigators to be increased by such factors as reduction in water-cement ratio,



increased fineness of cement, decreased  $C_3A$  content, and increased  $C_2S$  content. The present studies have shown that strength-heat relations may be definitely influenced by the addition of combinations of certain reagents.

The influence of HR-20 on the strength-heat ratio is shown in Table C. The strength data were taken from the results of concrete tests for the leanest mixes made with standard cement L; heat of hydration data were taken from tests made on neat cements. At all ages the strength-heat ratio is markedly increased

TABLE C

Age Days	Strength-Heat Ratio Lb. per sq. in. per cal. per gramme	
	Plain	HR-20
3	12	34
7	16	26
28	20	26
90	24	30

by HR-20; at the age of three days the ratio is almost three times that for the plain concrete, but the difference is less at the later ages.

The results of tests on the effect of the three combinations of active reagents on the compressive strength of concrete and on heat of hydration have brought out a further interesting relation. Since the reduction in water-cement ratio permitted by the use of HR-0, HR-10 and HR-20 reduced heat evolution (except HR-0 at three and seven days and HR-20 at 28 days and beyond) a reduction in heat evolution with an actual increase in strength is obtained. It follows from this that for a given strength the heat evolution can be decreased materially by the use of these materials. This relation, therefore, affords a means of controlling total heat evolution as well as the rate.

Freezing and thawing tests on concrete mixes containing HR-0 and HR-20 show that the durability of the concrete is enhanced by the use of these materials as would be expected from the reduction in water-cement ratio and other characteristics which they are known to have.

A limited number of tests on other properties of concrete were made. HR-0 appears to reduce the shrinkage slightly and HR-20 to increase it slightly. The addition of the three combinations of materials had some effect on the unit weight of the concrete. This amounted to an average reduction of 2 per cent. with a maximum reduction of 3.5 per cent. The use of the three materials showed a definite tendency to reduce bleeding or water-gain. Although no quantitative measurements were made, reduced water-gain was readily noticeable in all mixes, especially in the leaner mixes.

### Summary.

(1) The dispersing agent retarded the early rate of heat liberation of cement and decreased the total heat evolved up to 24 hours; it delayed the time of rapid heat evolution for  $C_3A$ , and greatly retarded the heat liberation of  $C_3S$ .

(2) The organic catalyst had a slight retarding effect on the early heat liberation of cement and  $C_3S$ . With  $C_3A$  it had a slight accelerating effect.

(3) The accelerator, calcium chloride, increased the maximum rate and total amount of heat liberated up to 24 hours. It had little effect on  $C_3A$ , but increased the rate and total amount of heat liberated by  $C_3S$ .

(4) The combination of dispersing agent and accelerator HR-0, designed for ordinary construction purposes, in general delayed the time of rapid heat evolution, increased slightly the total heat evolved up to seven days, and had no appreciable effect at 28 days. When used in concrete it reduced the water-cement ratio for a given workability, increased strength correspondingly, and improved durability with respect to freezing and thawing.

(5) The combination of dispersing agent, accelerator, and organic catalyst HR-10, also designed for ordinary construction purposes, generally retarded heat liberation up to three days but had little effect thereafter. In concrete it has about the same effect as HR-0 except that at later ages there was evidence of greater increases in strength.

(6) The combination of dispersing agent and organic catalyst HR-20 designed for work where heat evolution is important, greatly reduced the early rate of heat liberation but increased the total heat liberated at 28 and 110 days. In concrete, the strength at the very early ages was not impaired by HR-20, and at the later ages the strength was increased approximately in accord with the reduction in water-cement ratio permitted by its use.

It is possible to control the early rate of heat liberation of cement in almost any desired direction by the use of suitable combinations of active reagents.

<sup>1</sup> R. W. Carlson, "The Significance of Early Heat Liberation of Cement Paste," *Proceedings 17th Annual Meeting, Highway Research Board*, Dec., 1937.

<sup>2</sup> Carlson, R. W., and Forbrich, L. R., "Correlation of Methods for Measuring Heat of Hydration of Cement," *Ind. Eng. Chem. Anal.*, Ed. 10 (7), 382-6, 1938.

<sup>3</sup> Lerch, Wm., *Eng. News-Record*, 113, 523 (1934).

<sup>4</sup> Kelly, J. W., *Journal Amer. Concrete Inst., Proceedings*, Vol. 34, p. 573, June, 1938.

<sup>5</sup> Davis, R. E., "Final Report on Cement Investigations for Boulder Dam," U.S. Bureau of Reclamation, Denver, 1934.

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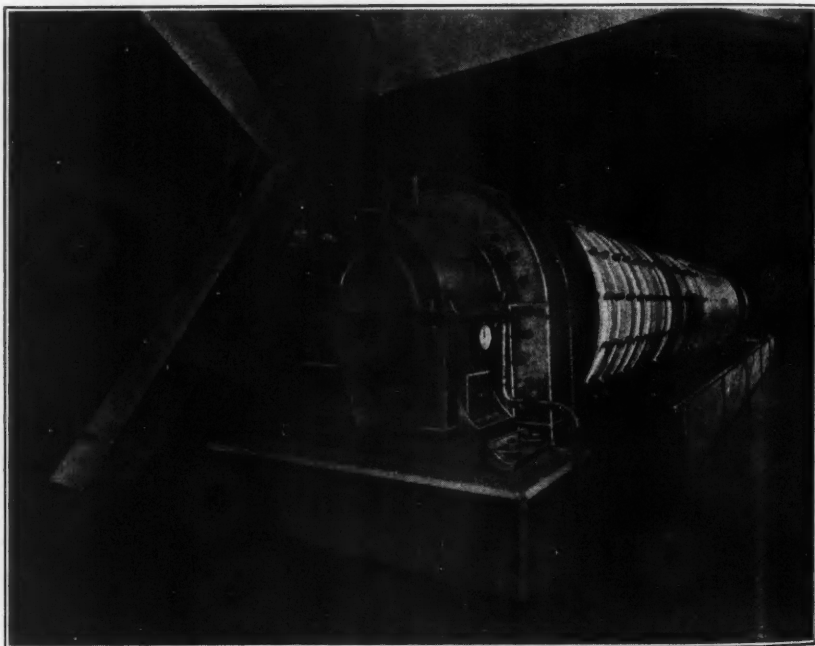
### Glass in Cement Clinker.

In Research Paper No. 1324 of the United States National Bureau of Standards, Mr. Herbert Insley describes a method of etching the polished surfaces of Portland cement clinkers with KOH solution. This method permits the detection of glass containing considerable iron which has been hitherto overlooked in microscopical examination. The results of quantitative microscopical analysis using this method are reported and compared with the results obtained by an older method.

The later results are practically identical with the earlier results for clinkers with  $Al_2O_3/Fe_2O_3$  ratios greater than 2.00, but for those with ratios less than 2.00 the later results indicate more glass and less  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$  than the earlier results. The quantitative results for glass by the later microscopical method are more nearly in agreement with the results by an independent method involving the determination of heat-of-solution.

## Combination Tube Mill

The illustration below shows a multi-chamber combination tube mill supplied by Messrs. Ernest Newell and Co., Ltd., of Misterton, Doncaster, for grinding high-alumina cement at the works of the Lafarge Aluminous Cement Co., Ltd., at West Thurrock. This machine is 39 ft. long by 7 ft. 3 in. diameter, and is made in sizes up to 45 ft. by 8 ft. It is fitted with concentric drive, "Flexic" torsion shaft and couplings, and "Cascade" visible oil lubrication to the main bearings. The shell, end plates, and the housings of the main bearings are fabricated throughout by the maker's electric welding process. It is claimed that the "Cascade" system of lubrication reduces power consumption and increases the life of the bearings, as the trunnions are supplied with a continuous stream of cascading oil. The three or four compartments into which the machines are divided are separated by diaphragm plates, and each compartment has a different type of shell lining and ball charge to suit the different conditions of grinding. The drive is by electric motor through a double-reduction totally-enclosed helical gear and "Flexic" torsion shaft and couplings. This type of machine is designed for the wet or dry grinding of any hard or refractory material; aluminous-cement clinker, on which the machine shown in our illustration is employed, is one of the hardest materials for which grinding machines are used.



## Re-use of Lime

THE re-use of lime in the paper and sugar industries is described by Mr. Oliver Bowles, of the United States Bureau of Mines, in the January, 1941, number of "Pit and Quarry." In these processes, states Mr. Bowles, the re-use of lime is not limited to a single time but is repeated in recurring cycles of chemical reaction. The lime, while performing certain functions, is recarbonated, and the product thus formed, which may be termed artificial or synthetic limestone, is recalined to lime, which is again used in the process.

In the paper industry chemical pulp is prepared from soft woods by the soda process, which involves digestion of wood chips with caustic soda. The soda liquor separated from the pulp is concentrated, evaporated to dryness, and the ash leached for its soda content. It becomes carbonated during the process and is converted into caustic soda ready for re-use by treating it with lime. The reaction is as follows:  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 = 2\text{NaOH} + \text{CaCO}_3$ . The calcium carbonate settles out as a sludge, which is calcined into lime and is then available for re-use.

The beet-sugar industry is a large consumer of limestone, which the sugar companies calcine in their own plants because they wish to recover the  $\text{CO}_2$  for



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use in the operation. About 620,000 tons of limestone (equivalent to more than 300,000 tons of lime) are used each year in sugar factories in the United States. The Steffen reaction involves the use of finely powdered quicklime, which precipitates sucrose from an aqueous solution of beet molasses. After the reaction is complete the addition of carbon dioxide converts the lime into calcium carbonate, which precipitates and is removed by filtering. Filter cake is recalcined less extensively in the sugar than in the paper industry, but recently a continuous process has been perfected whereby recalcination will probably become a more important factor. The Holly Sugar Company, in co-operation with the Colorado Iron Works, has developed a hearth-type gas-fired muffle furnace, which produces from the filter cake a gas containing approximately 30 per cent.  $\text{CO}_2$  and a lime more active than that obtained from freshly burned limestone. Though scarcely beyond the experimental stage, the new equipment bears promise of a decided advance in the re-use of calcium carbonate sludge at beet-sugar mills.

Another unusual re-use of lime is that involved in alkali manufacture. The Michigan Alkali Company uses large quantities of limestone in making soda ash and caustic soda from common salt. In making soda ash the principal by-product is calcium chloride, which is largely a waste material. However, in making caustic soda from the soda ash, lime is used and large quantities of calcium carbonate sludge are produced. Instead of recalcining this material to lime, as in the paper and beet-sugar industries, it is used for the manufacture of Portland cement in an adjoining plant.

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